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CONTENTS

Tamaz R. Agladze*

THE MODERN UNDERSTANDING OF THE CORROSION AND PASSIVATION PROCESSES OF IRON GROUP METALS

1. INTRODUCTION

Electrode processes at transition metals are traditionally envisaged from the point of view of the characteristic state of the surface metal–solution interface. These states are defined as active, prepassive transition, passive etc. and are commonly identified by the shape of potential–current dependencies. It is generally assumed that under equilibrium conditions metals are in active state, which usually means that under activation control potential–current relationship follows Tafel law. The steady state cathodic deposition and anodic dissolution Tafel lines of iron group metals (curves AB and CD respectively, at Fig. 1), when extrapolated intercept at the corresponding values of equilibrium potentials, calculated from thermodynamic data.
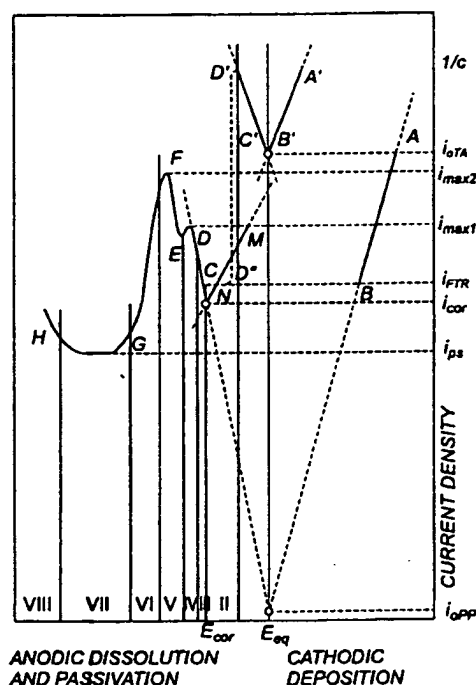
Fig. 1. *Schematic polarization curves of iron group metals in acid solutions. Ranges: I – TA; II – FT; III – PP; IV – Second transition (ST); V – Prepassive; VI – Passive layer formation; VII – Passive; VIII – Transpassive. AB–A'B' – Tafel curves for deposition reaction in PP and TA states, respectively. CD–C'D' – Tafel curves for dissolution reaction in PP and TA states, respectively. D''C – dissolution curve in FTR. MN – Cathodic curve for hydrogen evolution reaction*

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Thus the values of current densities, estimated from these interceptions, characterize exchange rates (i_0) of the corresponding M(II)/M electrode systems. As follows from Table 1 for iron group metals these values are of the order of $10^{-13} \div 10^{-9}$ A · cm^{-2} and are significantly lower than similar data for other transition metals. Strong inhibition of electrode reactions is apparently the consequence of the presence of the inhibiting layer, stable even at equilibrium potentials.

Table 1. The Rates of Electrode Reactions at Amalgam and Solid Electrodes in True Active and Primary Passive States (A · cm^{-2}, -298 K) [1]

Electrode system	Amalgam electrode	Solid electrode	
		PP state	TA state
Fe(II)/Fe	$3 \cdot 10^{-13}$	10^{-10}	10^{-1} (398 K)
Co(II)/Co	$\sim 10^{-13}$	$\sim 10^{-8}$	10^{-1} (423 K)
Ni(II)/Ni		$10^{-8} \div 10^{-10}$	10^{-1} (473 K)
Ni(I)/Ni	$2 \cdot 10^{-10}$	$1.9 \cdot 10^{-4}$	$\sim 10^{-3}$
Ni(II)/Ni(I)	$1.3 \cdot 10^{-7}$	–	–.
Mn(II)/Mn		$6 \cdot 10^{-3}$	–
Mn(I)/Mn	$5 \cdot 10^{-4}$	–	–
Mn(II)/Mn(I)	$1 \cdot 10^{-1}$	–	–
Cd(II)/Cd	–	–	$5.8 \cdot 10^{-2}$

2. KINETICS OF THE DISSOLUTION REACTION IN TRUE ACTIVE STATES

Strong activation of electrode reactions in "active" state by means of constant or discrete surface renewal of surface relaxation technique indicates that the so called "active" state actually refers to the state, when the surface is covered by the inhibiting layer [1–4]. The similar conclusion can be drawn from the results obtained in high temperature aqueous solutions [5, 6]. At temperatures higher than the boiling temperature of water, the exchange current density of Fe,Ni and Co electrodes increases much greater than it could be predicted on the basis of a simple effect of temperature on the activation energy of the electrode reaction. Differences in overvoltages of these electrodes diminish, vanishing at $T > T_c$, where T_c is the critical temperature, dependent on the nature of metal (Fig. 2).

Under activation conditions, reaction rates become independent of the solution pH, nature and concentration of anions and also of the presence of surface active substances. The values of standard exchange current densities of these metal electrodes tend to become closer to each other, yielding the maximal value of about 0.1 A · cm^{-2}, which is of the same order of magnitude as the corresponding values of transition metals, characterized by low overvoltages of deposition–dissolution reactions. These results were interpreted in terms of

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strong retardation of electrode reactions of iron group metals as a result of adsorption of alien inhibiting species at ambient temperatures and activation of the metal surface due to the temperature stimulated desorption of these species. It was found that irrespective of the way of the activation of Ni electrode (either by introducing fresh metal surface of elevating the temperature of the liquid phase) the result is the transition from non-equilibrium conditions ($i_o \ll i_{cor}$) to equilibrium ones ($i_{cor} \ll i_o$), which is manifested in the transition of corrosion potentials to Nernstian ones.

To distinguish two limiting states of the surface, it is convenient to introduce the notions of true active (TA) and primary passive (PP) states. When bare metal surface is introduced instantaneously into the aqueous solution of corresponding metal salts, the spectrum of electrode potentials and currents (at constant potential), reflecting the relaxation of the electrode surface from TA to PP states, was observed. It was found that the equilibrium potential of Ni(II)/Ni electrode was established at the interface for shot period of time t_c. Since the rate of Ni deposition reaction at $t < t_c$

Fig. 2. *Variation of the cathodic and anodic overvoltages of nickel, cobalt and iron electrodes with temperature in 1 N MeSO$_4$ (pH 1.5) at the current density 10 mA · cm^{-2}*

significantly exceeds the rate of hydrogen evolution reaction, it may be assumed the fast cathodic and anodic. Tafel lines characterize the kinetics of the deposition–dissolution reactions and hence the values i_o, estimated from the extrapolation of these lines at $\eta = 0$, are equal – or at least close – to the true values of exchange current densities of Ni(II)/Ni electrode system (Fig. 1). It follows from Table 2 that the kinetic parameters, obtained at fresh surface at ambient temperatures and at elevated temperatures are in general agreement with each other: cathodic and anodic curves are symmetrical, apparent transfer coefficients are close to 0.5 and their sum is twice as small as the total number of electrons involved in

Table 2. Kinetic Parameters of Ni(II)/Ni Electrode [1–5]

Parameter	Theory	Experiment:		
		Fresh surface	298 K	430 K
		NiF$_2$ + NaF	NiSO$_4$ + Na$_2$SO$_4$	NiSO$_4$
$\partial\eta/\partial \lg i_c$	$2.3RT/\alpha_2 F$	(0.120 ± 0.014) V	(0.120 ± 0.014) V	(0.115 ± 0.020) V
$\partial\eta/\partial \lg i_a$	$2.3RT/\beta_2 F$	(0.120 ± 0.014) V	(0.120 ± 0.014) V	(0.095 ± 0.040) V
$\partial \lg i_c/\partial \lg a_{Ni}^{2+}$	1.0	0.94	0.70	–
$\partial \lg i_a/\partial \lg a_{Ni}^{2+}$	0.5	0.35	0.35	0.30
$\partial \lg i_o/\partial \lg a_{Ni}^{2+}$	$(1 + \beta_2)/2$	0.65	0.45	0.55

the overall electrode process*. Further it follows from these data that not only the rate of the cathodic reaction, but also the rate of the anodic one, though to a minor degree, grows with an increase in Ni(II) concentration. On the basis of these kinetic parameters it was assumed that the overall electrode reaction involves two elementary consecutive charge transfer steps

$$Ni \Leftrightarrow Ni(I) + e, i_{01} \qquad (1)$$

$$Ni(I) \Leftrightarrow Ni(II) + e, i_{02} \qquad (2)$$

and a parallel heterogeneous disproportionation reaction of unstable intermediate:

$$2Ni(I) \Leftrightarrow Ni + Ni(II), i_D \qquad (3)$$

Taking into account the weak effect of pH on i_o it was assumed that a minor part of the intermediate can be oxidized also in the homogeneous chemical reaction:

$$Ni(I) + H_3O^+ \rightarrow Ni(II) + H^0 + H_2O, i_c \qquad (4)$$

Theoretical and experimental kinetic parameters are in agreement under the assumption that $i_{01} << 02 < i_D$, $i_D >> i_c$, and $\alpha = \beta = 0.5$, i.e. that the overall electrode process, controlled by the rate of step (1) actually proceeds via redox reaction (2) and heterogeneous equilibrium (3). Such ratio of the rates of the elementary steps seems to be reasonable, since the solvation and de-solvation of Ni(I) is expected to provide the highest activation barrier, while both species participating in step (2) are in a solvated from, and rapid electron exchange between them is expected. According to the proposed reaction scheme, the equilibrium activity of the intermediate depends on the activity of Ni(II) ions by the equation:

$$a_{Ni(I)} = K^{-\frac{1}{2}} \cdot (a_{Ni(II)})^{\frac{1}{2}} \qquad (5)$$

and the reaction rate is

$$i = (K')^{-\frac{1}{2}} \cdot (a_{Ni(II)})^{\frac{1}{2}} \cdot \exp(\beta_2 \cdot FE/RT) \qquad (6)$$

while exchange current density is determined by the equation:

$$I_o = K'' \cdot (a_{Ni(II)})^{(1+\beta_2)/2} \qquad (7)$$

The validity of scheme (1–4) was proved by independent measurements of the anodic current at the "indicator" platinum electrode, placed close to the rotating scraped nickel cylinder. In accordance with equation (5) in was found that the increment in anodic current flowing trough the Pt electrode is apparently due to the oxidation of Ni(I) ions and varies linearly with the square root of the concentration of Ni(II) ions.

Some comments should be made concerning the above results.

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*The variation of the apparent transfer coefficients with temperature deviates from the one predicted by Folmer–Tafel mechanism. The possible reasons of the "anomalous" temperature independence of the Tafel slopes are discussed elsewhere (e.g. [1])

- The majority of data on the kinetics of the dissolution and deposition of iron group metals is obtained under conditions when the M(II)/M electrode systems behave as totally irreversible, even in the vicinity of E_{eq}. The reason for this seems to be the formation of a surface layer, which strongly inhibits metal–solution exchange reactions.

- The dissolution reaction could be referred to the stable TA state at equilibrium potential and at relatively low anodic overvoltages at elevated temperatures.

- The scheme (1–4) implies a transfer of metal atoms into the solution via the formation of simple hydrated intermediate metal ions and vice versa. This assumption to a certain extent contradicts the generally accepted idea about the stabilization of reaction intermediates by adsorbed hydroxide ions, which is based on the experimentally observed pH dependence of the rate of the electrode reactions of iron group metals in aqueous solutions at ambient temperatures.

- Ni(II)/Ni(Hg) electrode reaction, under equilibrium conditions and at low overvoltages, follows via steps (1, 2), with an exchange current density of step (1) of more than two orders of magnitude lower than the corresponding value for step (2) (Table 1). The same ratio of the rates of the elementary steps was assumed for Ni(II)/Ni electrode. However, the exchange of a solid nickel electrode with Nickel(I) ions proceeds at the rates of a liquid one. Bearing in mind that the hydration energy of Ni(I) ions in both solutions is almost similar, the only reasonable conclusion can be drawn that great differences in reaction rates may be attributed to the catalysis of reaction (1) at solid nickel, which is apparently caused by chemisorption of intermediate ions at the interface. Following this approach, steps (1) and (2) should be modified as

$$Ni \Leftrightarrow Ni(I)_{ads} + e \qquad\qquad (1')$$

$$Ni(I)_{ads} \Leftrightarrow Ni(II) + e \qquad\qquad (2')$$

under the assumption that the surface coverage by adsorbed intermediate in low.

- It seems that the widely accepted idea about the facilitation of the electrode reaction as a result of the reduction of the activation energy by surface intermediate complexes involving the components of the liquid phase, is probably not as universal as it seems to be. Generally speaking, there is not much reason in the obligatory stabilization of the adsorbed intermediates through the surface complexation reaction. Moreover, examples of strong chemisorption of simple metal atoms and ions from gas phase at metal substrates are well known [7]. Ionized metal atoms can be stable at the interface even in the absence of adsorbed solution components [8, 9]. It seems probable that the chemisorption of any solution component results in the lowering of the catalytic effect provided by the solid surface. The other extreme seems to be amalgam electrodes which display low exchange rates, apparently due to negligibly low adsorption energy of intermediates at liquid metals. It might be that the exchange of solid electrode with the solution via "surface complex formation" mechanism is most characteristic of the electrodes covered by primary passive film and exhibiting intermediate (between true active and true passive states) reaction rates.

- Remarks also should be made on the correctness of the widely used procedure of the determination of the activation energy of electrode reactions from Arrhenius plots. This

procedure requires the constancy of all parameters, in both liquid and solid phases, excluding the temperature of the electrode system. However, as it was demonstrated above, in the case of iron group metals the variation in temperature results not only in the change in the height of the activation barrier, but also in a significant change in the activity of surface layer of the solid phase. Hence, the energy of activation calculated from Arrhenius plots is erroneous and should be corrected for the contribution of the corresponding change in the activity of the solid phase at the interface.

3. PRIMARY PASSIVE FILM

Potential regions where the deposition–dissolution reactions of most transition metals occur, are more negative than the equilibrium potential of the electrode systems where the corresponding metal is in the lowest state of oxidation. Therefore, the possibility of the inhibition of the electrode reaction due to the formation of a stable metal oxide phase at the interface should be excluded for thermodynamic reasons. However, the formation in this potential region of a layer of adsorbed solvent molecules and ions is possible. Moreover, there is every reason to expect that specific metal–solvent interactions largely contribute to the inhibition effect.

Certain conclusions on the nature of the PP film at nickel electrode can be drawn on the basis of the value of t_c, under the assumption that the latter is to some extent is a measure of the surface layer. A decrease in t_c con be considered as indirect evidence of a decrease in the activity of surface sites, involved in exchange reaction (1', 2'), due to the passivating effect increases in the same order as the surface activity of anions which in turn is greater at lower pH-s [2–4]. Thus, it is reasonable to assume that the primary passive film consists mainly of adsorbed hydroxide groups and anions adsorbed either according to solvent displacement or hydrogen-bonding mechanisms.

The formation of PP film obviously must result in a decrease in the surface activity of the reaction intermediate Ni(I). Taking into account equations (5–7) and assuming that equilibrium activity of the intermediate is proportional to the fraction of the surface sites, free from alien particles, i.e.

$$a_{Ni(I)} = K_{eq} \cdot \{a_{Ni(II)}\}^{1/2} \cdot (1 - \Theta)^{1/2} \tag{8}$$

it can be deduced that

$$i_o = K_a \cdot \{a_{Ni(II)}\}^{1/4} \cdot (1 - \Theta)^{1/4} \tag{9}$$

and

$$i_o / i_{0, TA} = (1 = \Theta)^{1/4} \tag{10}$$

Equation (10) can be used to analyze the kinetics of the passivation of true active surface of metal. Fig. 3 shows adsorption isotherms calculated on the basis of $i_{0, TA}$ values determined by the extrapolation of (i, t) curves at $t = 0$. It follows from these data that at

relatively short times of exposition of the fresh surface to the solution ($t < 100$ msec), Θ increases with time, reaching the limiting values at longer times of contact. This effect is enhanced when small amounts of sulphate ions are added to the fluoride solution. Similar effects are observed when potential is shifted to more positive values. An increase in Θ results in the deviation of the anodic curves from Tafel law at relatively high overvoltages and in a decrease in anodic current densities up to the values lower than the corresponding cathodic current densities provided by hydrogen evolution reaction. Hence, at high anodic over-

Fig. 3. *Variation of the coverage by primary passive film in time. 0.05 M NiF$_2$ + 0.45 M NaF (1) and 0.05 M NiF$_2$ + 0.45 M NaF + 5·10^{-3} M Na$_2$SO$_4$ (2)*

voltages, a part of the anodic curve is shadowed by the cathodic polarization curve. For this reason, the kinetics of the dissolution in the region, which may be defined as first transition region FTR* spread from TA to PP states (region D'D''C, Fig. 1) can be studied only by means of direct analytical control of the amount of the dissolved metal.
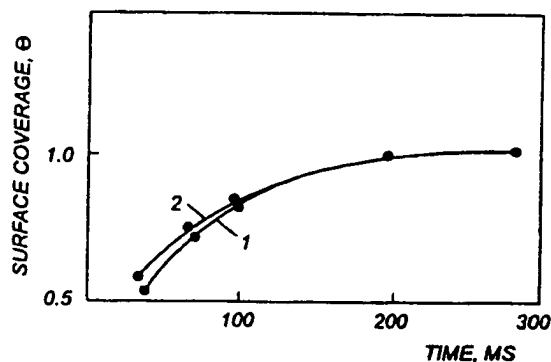
4. THE KINETICS OF THE DISSOLUTION IN THE FIRST TRANSITION REGION

The dissolution of transition metals in the potential region negative to corrosion potential which corresponds to the FTR, displayed a number of peculiarities. The majority of the transition metals exhibit relatively high dissolution rates, which are independent of potential and of the nature and concentration of the anions and are accelerated by acidification and heating of the solution. These effects were discovered for Fe and Cr [10], Ni [12], Co [13, 14], Mn [15, 16] and Zn [19] electrodes (Fig. 4). Though
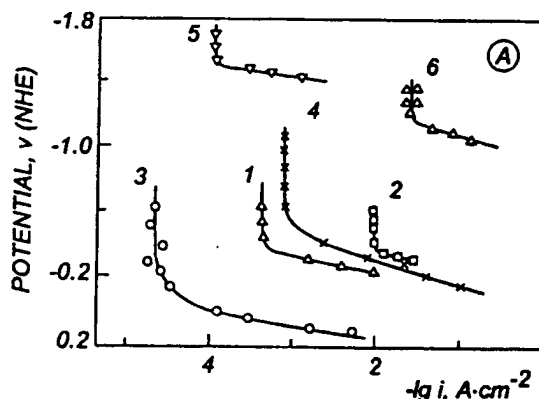

Fig. 4. *Dependence of the dissolution rate of iron (1), chromium (2), nickel (3), aluminum (4), zinc (5) and manganese (6) on potential in: 1–3 – 1N H$_2$SO$_4$; 4 – 1N H$_2$SO$_4$ + 0.1N NaCl; 5 – 1N H$_2$SO$_4$ + 0.5N Na$_2$SO$_4$; 1–3 – 50°C; 4–6 – 25°C [18]*

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* To differentiate transition region from TA to PP state from "active to passive" transition region, it is convenient to define the former as the first transition region (Fig. 1).

the dissolution rate of transition metals displays the pH dependence opposite to that which is commonly observed in a more positive (PP) region of potentials for iron group metals, different positive reaction orders in respect to H^+ ions were observed: $n = 2$ (Mn), $n = 1$ (Cr, Co), and $n = 0.2$–0.7 (depending on the purity of Fe). It was also shown that, under similar experimental conditions, potential-independent dissolution rate of electrodeposited Co with the texture <1010> is 3 times higher than that for <1120> and 25 times for <0001> – indicating an important role of surface morphology and, particularly, of the density of grain boundaries. The presence of impurities, e.g. carbon, also provides the accelerating effect [18]. At given solution pH and temperature, the rate of "anomalous" dissolution decreases in the order Mn, Co, Fe, and Ni.

The various possible explanations of the described effects were analyzed. It was assumed that anomalous dissolution in cathodic region can be attributed to:

- dissolution of metals via potential-independent chemical reaction [10],
- influence of the secondary effects, such as local pH changes, hydride formation, screening of the surface by hydrogen gas bubbles [19], inculcation of alkaline metals [20], mechanical disintegration due to hydrogen penetration into the metal lattice [21] or increased negative charge of the surface of the electrode,
- redistribution of the potential drop in a dense part of the double layer, caused by electrostatic screening of the metal surface by chemisorbed water molecules [22].

The critical analysis of the validity of proposed mechanisms is given in Ref. 1.

According to the model of dissolution, discussed above, the region of low overvoltages of h.e.r. corresponds to the first transition region, where the limiting coverage of the surface sites by PP film, consisting basically of $M(OH)_{ads}$ species, is assumed. An assumption about the presence of the adsorbed PP film in this potential region inevitably leads to the idea about the interference of the passivation and hydrogen evolution reactions. Taking into account the results of the isotopic kinetic effect for h.e.r. at transition metals [23, 24] the cathodic electrochemical desorption step can be proposed

$$M(OH)^-ads + 2\ H_3O^+ + 2e \rightarrow M + H_2 + 2\ H_2O + OH^- \qquad (11)$$
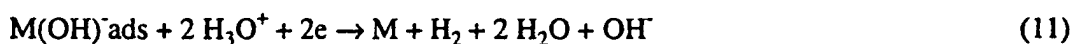
The steady-state concentration of surface active sites in this case will be determined by the balance of the rates of reactions of metal dissolution (1', 2'), adsorption and desorption of passivating film. Taking into account that reactions (1', 2') and (11) commonly follow Tafel lines with similar slopes (120 mV dec^{-1}), and that potential exerts opposite effects on the rates of these reactions, one can expect a compensation effect, due to which the overall dissolution reaction will not depend on potential in the FTR.

The compensation model also adequately accounts for a number of peculiarities of anomalous dissolution. The acceleration of the dissolution rate with scouring or with an increase in the concentration of hydroxonium ions, as well as any proton donor (e.g. NH_4^+ ions [16] or H_2O_2 molecules [25]) is apparently due to a rise in the rate of desorption step (11), which is accompanied by an increase in the surface concentration of active sites involved in the dissolution reaction (1', 2'). The localized character of dissolution, strong effect of the surface structure and morphology [14, 21] as well as of contaminants like carbon [18, 21], is apparently the result of the sensitivity of the overvoltage of the reaction (11) to these factors.

It is obvious that h.e.r. has an effect of great importance, and any model of the dissolution of transition metals under cathodic polarization which ignores the consequences of this is not trustworthy. It is reasonable to assume that hydride formation is completely, or at last partially, responsible for the effect of the excess of the analytically determined amount of dissolved metal and hydrogen gas over the values calculated from the corresponding anodic and cathodic currents – the effects which are usually observed at low pHs or elevated temperatures, e.g. under conditions promoting the formation and decomposition of surface hydrides.

5. THE KINETICS OF ELECTRODE REACTION AT IRON GROUP METALS IN PRIMARY PASSIVE STATE

The kinetics of iron, nickel and cobalt electrodes was in the focus of a great amount of studies over the past fifty years [8, 26].

According to the generalized model of electrode reactions discussed above, the region of potentials positive to corrosion potential corresponds to the dissolution of iron group metals which are already covered by primary passive film consisting mainly of absorbed hydroxide groups and anions. It can be assumed that the acceleration of the dissolution reaction with anodic polarization may be attributed to the contribution of the absorbed hydroxide ions in the formation of activated complexes involving surface atoms under the effect of an increasing positive charge of the interface. Such complexes should apparently stimulate the shifting of surface atoms from their equilibrium state in the metal lattice and, thus, the lowering of the activation energy of the anodic process. In other words, the dissolution of metals will proceed via the formation of intermediate charge-transfer complexes, the presence of which is commonly assumed in the mechanisms of electrode reactions of iron group metals to explain the acceleration of electrode reactions with an increase in pH of the solution.

It is noteworthy that the generalized model predicts also the opposite effect of pH at a high concentration of hydroxonium ions due to a strong decrease in the overvoltage of desorption reaction (11), and a subsequent increase in the activity of surface active sites participating in anodic reactions. The model also assumes a possibility of the dissolution of the metals in the PP region via the formation of activated complexes, involving anions, incorporated in the PP layer. It seems, however, that the reactivity of such complexes is somewhat lower than of those formed by hydroxide ions. This can be in particular the reason for a decrease in exchange current density of iron electrode in the order of anions $ClO_4^- >$ $SO_4^{2-} > Cl^- > CH_3COO^- > NO_3^-$ [28]. It should be noted that a decrease in i_o follows generally the same line as t_c. The acceleration of the anodic reaction with an increase in the concentration of anions is apparently more probable at low pHs (when the surface concentration of hydroxide complexes is low), high concentration of anions and at high anodic overvoltages, which are conducive to the formation of activated charge transfer complexes, apparently less reactive than the corresponding complexes involving hydroxide ions.

According to the model described above, the steady-state surface coverage by adsorbed complexes at corrosion potential is determined by the kinetics of the reactions of adsorption and desorption of hydroxide, as well as by the reaction of anodic dissolution of metal, let alone a possible contribution in this reaction of anions and hydrides. Since the rates of all

these reactions are significantly affected by external (potential, temperature, pH etc.) and internal (surface structure and morphology, contaminants etc.) parameters of the system, one can expect a considerable uncertainty in the surface state of the electrode at the beginning of the "active" region – the effect which particularly can contribute to the controversy of experimental data on the kinetics of electrode reactions of iron, nickel and cobalt.

However, it seems that the arbitrariness in the choice of the initial state is somewhat limited by the similarity in the surface pretreatment routine in the majority of studies. It is probably due to this that the majority of experimental kinetic parameters of electrode reactions at iron group metals in PP state can be reduced to two main groups – those fitting the mechanism proposed originally by Heusler [27] and those fitting the mechanism proposed originally by Bockris, Drazic and Despic [28].

6. CONCLUSIONS

Iron group metals exhibit equilibrium behaviour only at temperatures above the critical values which are specific of the nature of metal. Equilibrium conditions can be also achieved for a short period of time at fresh metal surface. Deposition and dissolution processes under equilibrium and medium overvoltages proceed at the electrodes, which are in true active state, apparently via consecutive charge-transfer steps involving monovalency metal ions adsorbed at active sites, which may be associated with kinks of monatomic steps. Variation in the chemical nature of metal within the group does not seem to play an important role in equilibrium behaviour of the electrode, while the process of formation of primary passive layer, as well as of a stable oxide layer, is sensitive to the nature of metal. Susceptibility to the primary passivity increases in the order Fe, Co, Ni

The formation of primary passive film, consisting of adsorbed hydroxide ions and anions, results in a strong retardation of electrode reactions and in the deviation from equilibrium conditions. Susceptibility to the formation of primary passive film grows with a decrease in temperature and an increase in anodic overvoltage. Transition from true active to primary passive state is influenced by the hydrogen evolution reaction and hydride formation. It is probable that potential-independent "anomalous" dissolution of transition metals in the first transition region is a result of the compensation effect arising from the influence of potential, similar in value and opposite in direction, on the rates of metal dissolution and hydrogen evolution reaction involving components of primary passive film.

At ambient temperatures, iron group metals are totally irreversible. Deposition and dissolution reactions, which commonly are considered as "active", actually proceed at a certain coverage of the surface by primary film and with the participation of its components. The formation of charge-transfer intermediates is caused by the activation of the state of adsorbed species due to increased anodic and cathodic overvoltages. The reactivity of hydroxide surface complexes seems to by higher than that of haloid ones.

Complex electrode reactions at iron group metals can be treated as a single process which embraces all intermediate states – from true active to stable passive ones. The generalized model, based on this approach, seems to give an adequate phenomenological description of electrode behaviour under the assumption that the rate of the electrode process at given surface morphology and solution composition is determined by the variation in reactivity of surface intermediates with temperature and potential.

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